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# Inhibition of a Low-Pressure Flame

## by Halogen Atoms

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## ABSTRACT

An attempt was made to introduce chlorine atoms directly into a low-pressure acetylene—oxygen flame. The atoms were formed by flash photolysis of molecular chlorine contained in the reactant gases. Momentary inhibition of the acetylene flame was observed. The phenomenon was studied by means of high-speed photography, spectroscopy, and hot-wire anemometry. It was concluded that inhibition was being caused by a chlorinated acetylene rather than by chlorine atoms. Recommendations for improving the experimental setup are presented.

## I. INTRODUCTION

The consequences of adding a halogen or a halogenated hydrocarbon to a flame have been the subject of recent work by several investigators, including Rosser, et al. (Ref.1). In Rosser's work, it appeared that halogen atoms were formed in the flame and that they subsequently reacted to bring about a decrease in the flame speed. Since atoms had to be formed initially, the use of halogenated compounds required that a bond be broken before inhibition of the flame could take place. Because of their more favorable bond energies, brominated compounds were approximately seven times more effective as flame inhibitors than chlorinated or iodinated compounds.

To avoid the complication introduced by breaking halogen bonds, it was proposed by M. Gilbert that halogen atoms be added directly to the flame. In this

way the relative flame-quenching capabilities of the various halogen atoms might be determined.

In the present investigation a flash photolysis technique was utilized to introduce the halogen atoms directly into the flame. A low-pressure flame, stabilized on a quartz tube, was supplied with a mixture of fuel, oxygen, and chlorine. Immediately below the flame a doughnut-shaped krypton flash tube surrounded the quartz flameholder. Discharge of a capacitor through the krypton lamp produced a high-intensity flash of light which brought about dissociation of the molecular halogen. The resulting atoms were carried into the flame by the flow stream. Inhibition caused by the halogen atoms was investigated by means of high-speed photography, hot-wire anemometry, and spectroscopy.

## II. EXPERIMENTAL EQUIPMENT AND MEASUREMENT TECHNIQUES

### A. Low-Pressure Flame Equipment

The low-pressure flame was contained in the apparatus, shown in Fig. 1, designed by M. Gilbert (Ref. 2). A premixed acetylene-oxygen-chlorine flame<sup>1</sup> (to be called hereafter the acetylene flame), burning at a pressure of 10 mm Hg, was utilized during most of the work. A few experiments were undertaken using a methane flame.

The use of chlorine required a modification of Gilbert's original apparatus. To avoid corrosion effects,

$$\begin{array}{ll} \text{1 } \frac{\text{C}_2\text{H}_2}{\text{O}_2 + \text{Cl}_2} = 0.13 & \frac{\text{Cl}_2}{\text{O}_2} = 0.05 \end{array}$$

Flow velocity (10 mm Hg) = 500 cm/sec  
Diameter of quartz flameholder = 4.0 cm  
Total flow (STP) = 74.5 cc/sec

monel plumbing was added to serve as the chlorine feed line. In addition, it was necessary to calibrate the flow meters for chlorine without actually using chlorine. This was accomplished for each meter as follows: A series of calibrations were made with gases having increasing molecular weights ( $\text{H}_2$ ,  $\text{CH}_4$ , air,  $\text{O}_2$ ,  $\text{C}_4\text{H}_{10}$ ). A graph of flow rate at a fixed graduation on the flow meter versus the molecular weight of the gas was then extrapolated to a molecular weight of 71 ( $\text{Cl}_2$ ). The result of carrying out the above process for each of several flow meter graduations was a graph of extrapolated chlorine flow rate versus the flow meter divisions.

The use of chlorine also created a problem in keeping the 35 gallons of vacuum-pump oil clean, for the chlorine charred the oil badly. Initially an attempt was made to filter the chlorine and chlorinated pro-

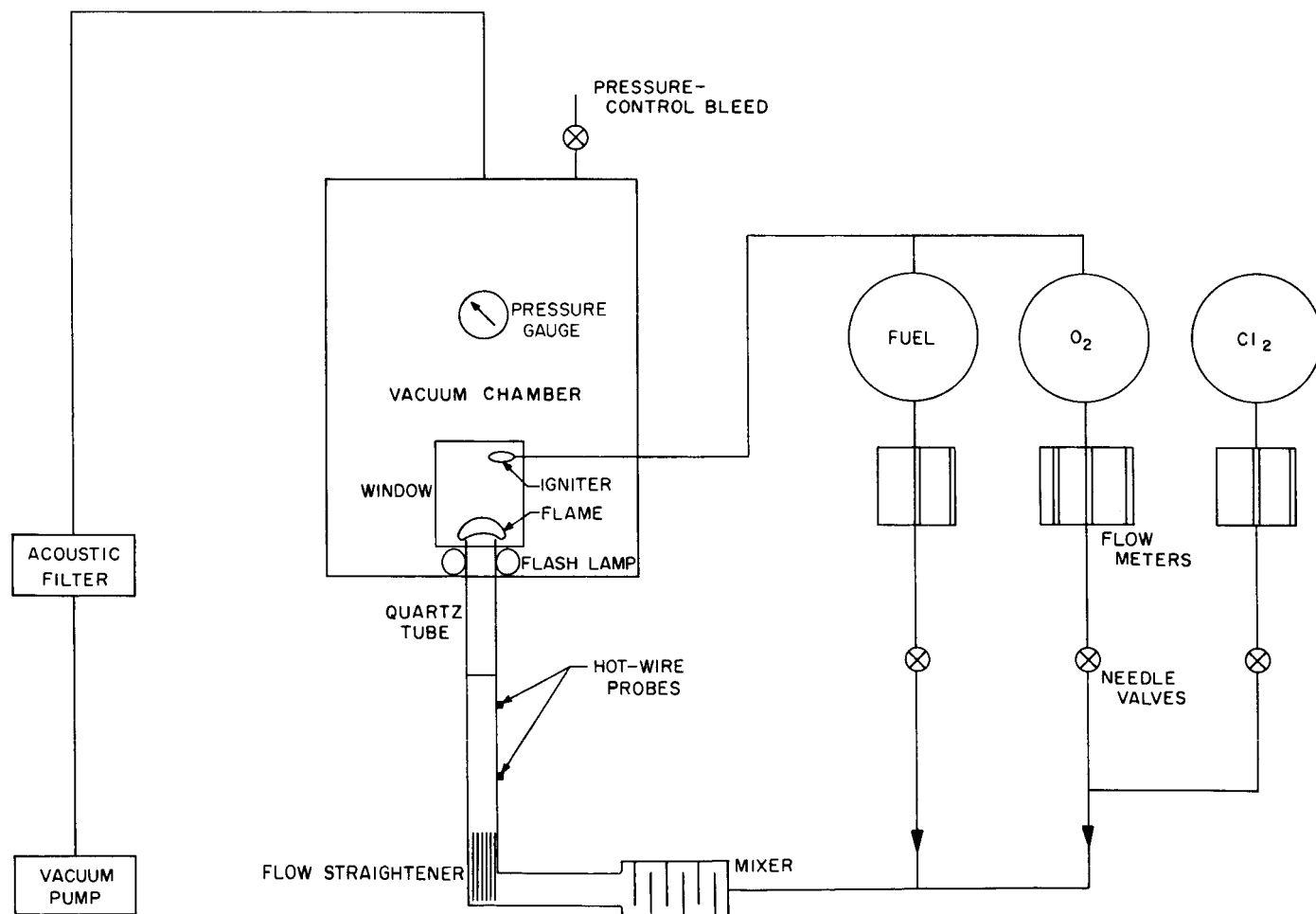


Fig. 1. Low-pressure-flame apparatus

ducts from the flame exhaust before they could reach the vacuum pump. Ion exchange resins were used to do the filtering, but they proved ineffectual in that only a fraction of the chlorine was removed. For this reason, the filters were removed and the pump oil was changed after every run (about two hours). The Welch Duo-Seal oil was replaced by the less expensive Texaco Canopus D, which performed just as well. Slow pumpdown was encountered at first, but this was ascribed to outgassing of the scale formed by chlorine corrosion within the iron vacuum chamber, even though the chamber was protected by a coat of Glyptal.

### B. Flash Equipment

The flash lamp consisted of a 12-mm-OD quartz tube in the shape of a doughnut just large enough to fit around the quartz flameholder. The tubing was filled with krypton to a pressure of 60 mm Hg. Two 3-kv, 100-mf capacitors in parallel were discharged through the lamp. The resulting light was concentrated immediately below the flame by reflectors. The discharge was triggered by a high-voltage spark coil.

### C. Photomultiplier

An RCA 6810A photomultiplier tube was operated from an 1800-v battery supply and utilized a 4.7-meg load resistor. The photomultiplier was mounted in an evacuated, liquid-nitrogen-refrigerated, glass Dewar (Ref. 3), which was contained in a light-tight box. The output from the photomultiplier was fed to a Tektronix 545A oscilloscope and recorded photographically.

### D. Optical Path for Emission Spectroscopy

The light travelled from the flame to the photomultiplier in the following manner (see Fig. 2): The image of the flame was rotated 90 deg by mirrors so that the vertical slit on the monochromator could subtend horizontal regions of the flame (preheat and combustion zones). The collecting lens gathered the light from the rotator and focused it on the monochromator slit. Image size could be controlled by varying the position of the lens and by either increasing or decreasing the length of the optical path. The variation in path length was achieved by moving one or both of the 45-deg front-surfaced mirrors.

The monochromator itself was a Bausch and Lomb grating instrument blazed for 3000 Å. (Catalog No. 33-86-45-68, 500 mm, 600 grooves/mm,  $f/4.4$ , 33 Å/mm, 2–14000 Å). The wavelength could be preset to within 1 mμ.

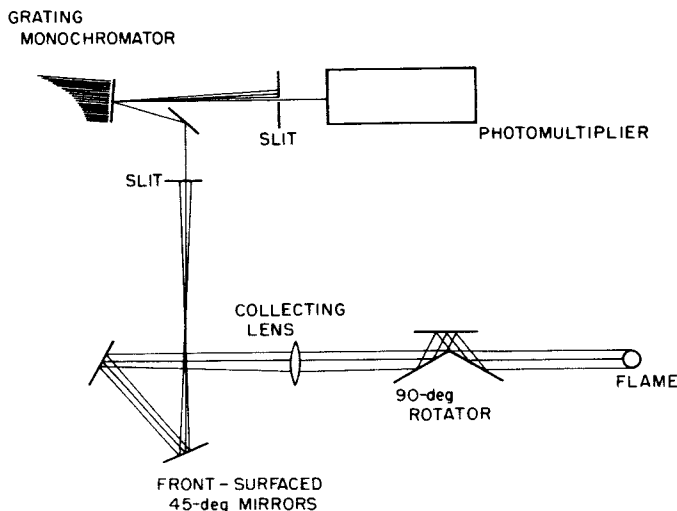


Fig. 2. Emission spectroscopy apparatus

### E. Optical Path for Absorption Spectroscopy

In order to measure the amount of atomic chlorine produced during the flash photolysis, the monochromator was replaced by a light source, a quartz sample cell (surrounded by the flash lamp), and a light filter encompassing the 3000–3500 Å region (see Fig. 3). In the spectral region noted above, chlorine molecules absorb, whereas chlorine atoms do not (Ref. 4). By using the photomultiplier to follow the transmitted light during and after the discharge of the flash lamp, it was possible to obtain a record of the percentage of chlorine converted to atoms and/or to chlorinated hydrocarbon.

### F. Spectrograph

A preliminary spectrum of the visible light emitted by the flame was obtained using a Cenco grating spectrograph which had a dispersion of 15.8 Å/mm.

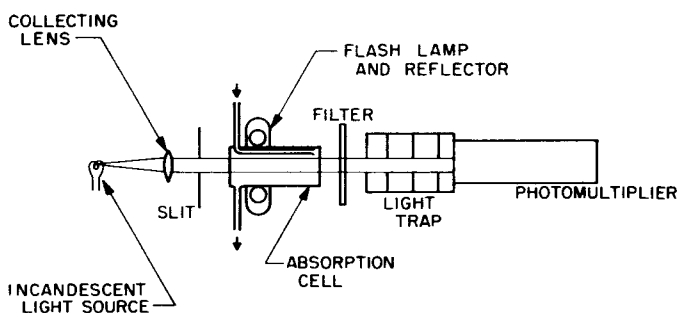


Fig. 3. Absorption spectroscopy apparatus

**G. Hot-Wire Anemometer**

The gasdynamic phenomena caused by the photodissociation of chlorine were investigated using a hot-wire apparatus. A 0.0001-in.-diameter platinum wire was mounted on a probe in the flow straightener at stations 18 in. and 30 in. below the flame (see Fig. 1). The voltage pulse was registered on an oscilloscope

**H. High-Speed Photography**

The combination of a Fastax camera with Ansco SuperHypan film produced slow-motion movies of

the flame inhibition. A speed of up to 6000 pictures per second was possible. Speed calibrations were obtained by means of a stroboscope.

**I. Schlieren System**

An optical schlieren system was constructed using the following components: a high-pressure mercury arc (BH-6), two concave, front-surfaced, parabolic mirrors (6-ft focal length), a knife edge, and a ground-glass viewing plate. It was hoped that, during the flame inhibition, the internal structure of the flame could be resolved.



### III. RESULTS

#### A. Photographic Results

##### 1. Acetylene Flame

A series of photographs taken with the Fastax camera is shown in Fig. 4. These pictures depict the sequence of events occurring in the acetylene flame immediately after triggering the flash lamp (2.4 kv, 200 mf).

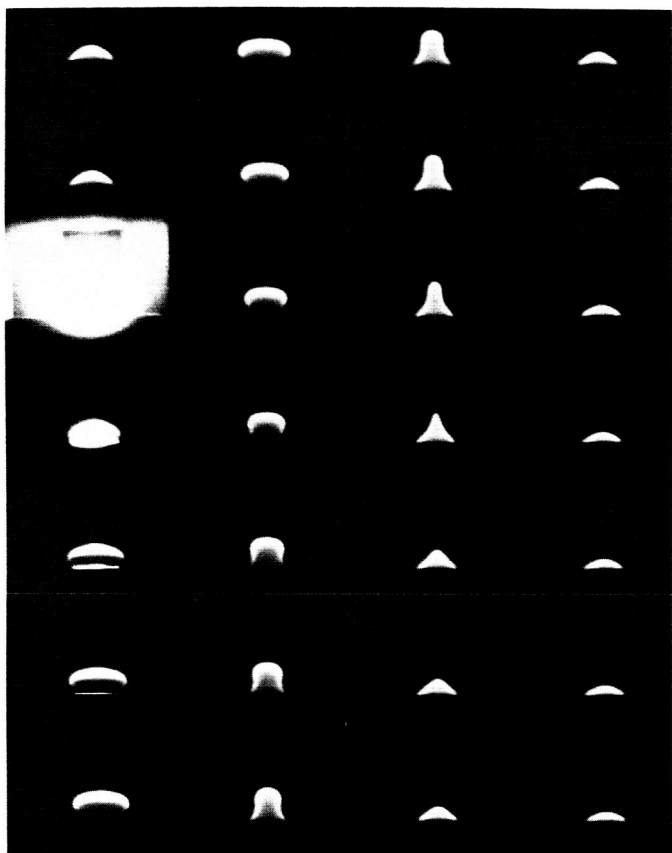


Fig. 4. Inhibited acetylene flame (Fastax photographs, 5000 pictures per second, flash lamp 1 cm below flame)

Irradiation of the chlorine took place 1 cm below the flame. The response of the flame was both immediate and violent. As inhibition of the reaction process took place, a reduction in the flame speed was noted. Consequently, the flame rose from its equilibrium position and simultaneously expanded. Return to the original position and shape occurred after approximately 5 msec. It appears that this interval measured photographically is low, for photomultiplier measurements of the variation in total light intensity (see Fig.

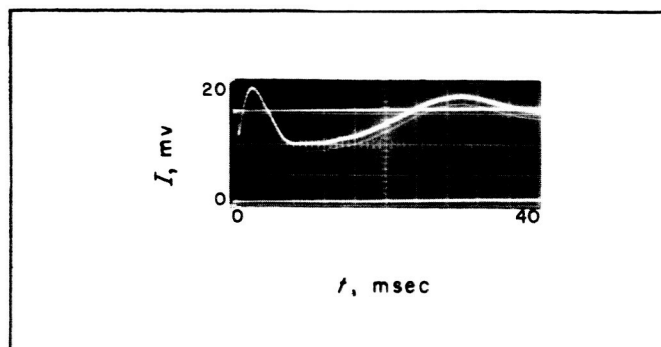


Fig. 5. Variation in light emission from the acetylene flame

5) indicated a recovery time of approximately 40 msec. The flowstream velocity was such that, assuming no reaction, the chlorine atoms would have passed through the flame front in 5 msec.<sup>2</sup>

When the flash lamp was shifted to a position 30 cm below the flame, an interesting phenomenon was observed (see Fig. 6). A time lag of only  $\frac{1}{2}$  msec between the flash and the beginning of flame inhibition indicated that light from the flash lamp reached the flame proper as well as the feed gases. The flame inhibition was more violent and of longer duration (12 msec)<sup>3</sup> than in the previous discussion concerning Fig. 5.

This relatively long duration of inhibition meant that a compound was forming between the chlorine atoms and the acetylene. Since the lifetime of chlorine atoms at 10 mm Hg is less than 10 msec (see Sec. III-D-1), the atoms alone could not have maintained inhibition for 12 msec or more. On the other hand, a compound formed at the flash lamp position would have taken approximately 30 msec ( $60/2$ , because of parabolic flow) to reach the flame. Hence, a chlorinated acetylene would explain the observed results. Thus, inhibition was caused by a halogenated hydrocarbon, as in Rosser's work, rather than by the atoms themselves.

<sup>2</sup>The value actually calculates out to 10 msec, but must be divided by a factor of 2 in order to allow for fully developed parabolic flow (from a private communication with H. Ford, JPL).

<sup>3</sup>Low by a factor of 8; cf. the previous discussion of light-intensity variations.

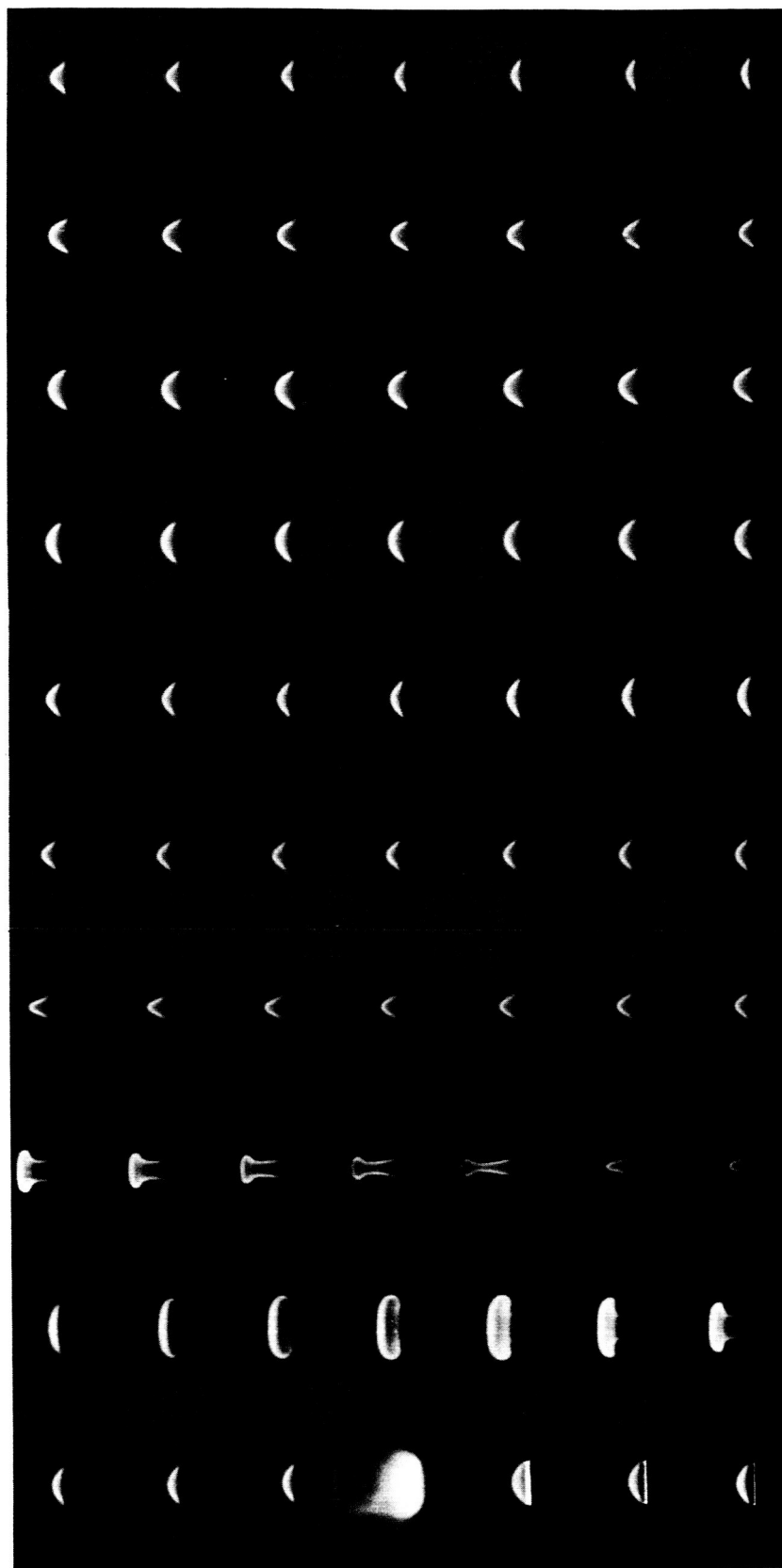


Fig. 6. Inhibited acetylene flame (Fastax photographs, 5000 pictures per second, flash lamp 30 cm below flame)

## 2. Methane Flame

The above conclusion was supported by work with a methane flame.<sup>4</sup> When a flash of 2.4 kv at 200 mf was utilized (see Fig. 7), it appeared that very little, if any, inhibition took place. The results indicated that before the atoms could enter the flame, they recom-

$$^4 \quad \frac{\text{CH}_4}{\text{O}_2 + \text{Cl}_2} = 0.42 \quad \frac{\text{Cl}_2}{\text{O}_2} = 0.052$$

Flow velocity (10 mm Hg) = 382 cm/sec  
Diameter of quartz flameholder = 4.0 cm  
Total flow (STP) = 60.1 cc/sec



Fig. 7. Inhibited methane flame (Fastax photographs, 5000 pictures per second)

bined rather than reacted with the methane; hence, there were no new halogenated species present in the flame to bring about inhibition.

## B. Gasdynamic Effects

The negative results obtained with the methane flame indicated that little or no interference due to gasdynamic effects was being encountered. In order to ensure that no pressure pulses were being created by the dissociation of the chlorine, the hot-wire anemometer was set up. With the flash lamp 1 cm below the top of the quartz tube, measurements of the variation in  $\rho U$  were made at the two probe stations ( $\rho$  and  $U$  are the flow-stream density and velocity). The noise of the lamp firing caused a large fluctuation in  $\rho U$ , but only a slight ripple was recorded during the time that the flame showed violent distortion. This ripple represented only a 1% ( $\pm 1\%$ ) variation in  $\rho U$  and, hence, could not have explained the behavior of the inhibited acetylene flame.

## C. Schlieren System Results

The optical schlieren system proved almost useless, for only the bare outline of the low-pressure acetylene flame could be distinguished. An electron schlieren system would have been required to study the density gradients within the flame.

## D. Spectroscopic Results

### 1. Absorption Spectroscopy

In order to resolve the question of compound formation between the chlorine atoms and acetylene, the acetylene, oxygen, and chlorine, both separately and mixed, were allowed to flow continuously through the quartz sample cell (see Fig. 4). They were then subjected to illumination from the flash lamp. Interference in recording results was encountered as a result of the decay of the flash lamp: the flash in this setup persisted 10 msec,<sup>5</sup> a length of time sufficient to mask the recombination of chlorine atoms. Consequently, during photolysis of chlorine alone, acetylene alone, and a mixture of chlorine and oxygen, no effect due to chlorine atom production was detected. However, when a mixture of chlorine and acetylene was photolyzed, a material formed which did not absorb light (3000–3500 Å) to as great an extent as chlorine. This new material persisted for 100 msec. A calculation based on

<sup>5</sup>Because of long electrical leads to the flash lamp.

flow rates indicated that the contents of the quartz absorption cell would ideally change every 150 msec. Since it was impossible to detect the recombination of chlorine atoms formed in pure chlorine, the new material could not have been atomic in nature. Hence, it must have been a compound produced by reaction between the chlorine atoms and the acetylene.

## 2. Emission Spectroscopy

Examination of the total light output of the inhibited acetylene flame included a study of the effects caused by sequential positioning of the slit so that different portions of the flame could be monitored. Measurements of light-intensity variations due to chlorine atoms were made at positions within the flame as well as above and below it. The resulting series of oscillograms (see Fig. 6 for an example) could not be explained by a change in flame intensity; rather, it appeared that the motion of the flame past the slit was being observed.

To decrease the effect of the flame motion, the image of the flame was enlarged. However, this decreased the light intensity falling on the slit, and before the effect of the motion could be eliminated, the sensitivity of the photomultiplier was overreached.

An attempt was made to use a ground-glass plate to exclude the effect of flame motion. The flame image was projected upon the ground glass, and any light striking this plate was then focused upon the photomultiplier. Hence, as long as the flame image did not move off the ground-glass plate, the total light intensity would be recorded. Preliminary tests of the system using an incandescent lamp as a source indicated that the setup was too unrefined to eliminate completely the effects of the flame motion.

Before the slit had been incorporated into the optical system, the total light output of the inhibited acetylene flame was examined as a function of pressure, flow velocity, fuel-oxidizer ratio, and chlorine-oxygen ratio. As noted previously, flame motion rather than light intensity was measured, but even this motion was a measure of the degree of flame inhibition.

Table 1 contains the results of varying such parameters as pressure and fuel-oxidizer ratio. The graphs of percentage change in light intensity versus energy supplied to the flash lamp are expressed in terms of the angle between the plotted points and the X-axis. A smaller angle indicates greater flame stability. These results are compatible with a mechanism of inhibition based upon either chlorine atoms or a chlorinated

Table 1. Variation in inhibition with flame parameters

Change with Velocity <sup>1</sup>		
Flow velocity, cm/sec	Slope of graph, <sup>2</sup> deg	Blowoff energy, joules supplied to flashlamp
306	53	488
400	35	1210
500	~ 30	...
Change with Pressure <sup>1</sup>		
Pressure, mm	Slope of graph, deg	
12	~ 30	
14	~ 25	
Change with Fuel Concentration <sup>1</sup>		
$\frac{C_2H_2}{O_2 + Cl_2}$	Slope of graph, deg	
0.126	~ 30	
0.200	> 30	
0.280	34	
Change with Chlorine Concentration <sup>1</sup>		
$\frac{Cl_2}{O_2}$	Slope of graph, deg	
0.050	11	
0.100	22	
0.160	~ 30	

<sup>1</sup>All other variables are fixed in value.

<sup>2</sup>X-axis, 25 joules per square; Y-axis, 5% per square.

acetylene. It has been shown that, in the present instance, a chlorinated acetylene is the cause of the flame inhibition. However, the data do not warrant a detailed discussion since it is impossible to relate them to the reaction kinetics.

## E. Spectrographic Results

The spectra (3000–7000 Å) of light emitted by the acetylene and methane flames are to be found in Fig. 8. The observed spectral lines were characteristic of CH, C<sub>2</sub>, and OH. No lines assignable to chlorine or its compounds were detected. As found by Rosser (Ref. 1), chlorine addition to a flame decreased the intensity of the OH line at 3060 Å.

Despite the failure to detect lines due to chlorine, it was decided to investigate the behavior of CH, C<sub>2</sub>, and OH during the period of flame inhibition. This was done by following the light output at specific wavelengths characteristic of each species.

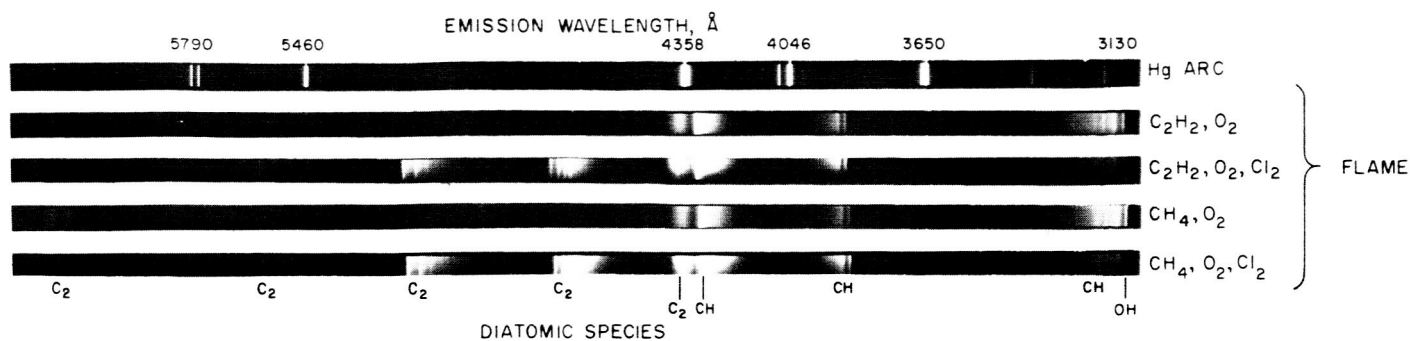


Fig. 8. Emission spectra from acetylene and methane flames

The light from the acetylene flame was introduced into the slit monochromator and thence into the photomultiplier. Results at several wavelengths proved to be qualitatively identical with each other and also with the results obtained using the total integrated light

spectrum (Fig. 6). The decay and recovery of all species seemed to be in phase. The explanation may lie in the motion of the flame image past the monochromator slit. Such motion would yield identical oscilloscope traces, no matter what wavelength was examined.

#### IV. CONCLUSIONS AND RECOMMENDATIONS

In the investigation of flame inhibition by chlorine atoms, it could not be shown that chlorine atoms were entering the flame. On the contrary, flame inhibition by a chlorinated hydrocarbon was shown to exist. Absorption spectroscopy, as well as the delay and inhibition times observed, supported the conclusion that an addition compound was formed between the acetylenic triple bonds and the chlorine atoms. Hence, halogenated hydrocarbons, as in Rosser's work, brought about the flame inhibition.

On the other hand, little or no reaction was encountered during the experiments using a methane flame. In this case, the difficulty of hydrogen abstraction prevented compound formation, thus leading to chlorine atom recombination. Hence, there was no change in the species entering the flame, and no inhibition.

Although this project has been discontinued at JPL, several recommendations for the successful conclusion of the work may be proposed. As presently

constructed, the apparatus is inadequate for the problem, since chlorine atoms do not reach the flame. A larger-diameter flameholder and a lower-pressure flame are necessary in order to increase the lifetime of the chlorine atoms.

It would be advisable to use a steady-state chlorine atom source rather than flash photolysis, for the transient motion of the flame is a major obstacle to carrying out emission spectroscopy.

Substitution of methane or hydrogen for acetylene is recommended in view of the compound formation between chlorine atoms and acetylene. Actual sampling of reaction products with a mass spectrograph or infrared spectrometer would be a useful adjunct to the procedures outlined above.

##### Acknowledgement

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## REFERENCES

1. Rosser, W. A., Wise, H., and Miller, J., *7th International Symposium on Combustion*, p. 175, 1958.
2. Gilbert, M., *The Investigation of Low-Pressure Flames*, Report No. 4-54, Jet Propulsion Laboratory, Pasadena, California, 1949.
3. Bronco, C. J., St. John, R. M., and Fowler, R. G., "Pyrex Demountable Photomultiplier Refrigerator," *Review of Scientific Instruments*, vol. 29:1145-46, 1958.
4. Porter, G., "Flash Photolysis and Spectroscopy. A New Method for the Study of Free Radical Reactions," *Proceedings of the Royal Society, Series A*, vol. 200:284, 1950.